

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

10/018020

INTERNATIONAL APPLICATION NO.
PCT/JP00/04793INTERNATIONAL FILING DATE
July 17, 2000PRIORITY DATE CLAIMED
July 21, 1999TITLE OF INVENTION
LITHIUM BATTERY

APPLICANT(S) FOR DO/EO/US

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Seijiro OCHIAI Toshiyuki WATANABE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. is attached hereto (required only if not communicated by the International Bureau).
 - b. has been communicated by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. is attached hereto.
 - b. has been previously submitted under 35 U.S.C. 154(d)(4).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. are attached hereto (required only if not communicated by the International Bureau).
 - b. have been communicated by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. A **FIRST** preliminary amendment.
16. A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. A substitute specification.
18. A change of power of attorney and/or address letter.
19. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. Certificate of Mailing by Express Mail
23. Other items or information:

PCT Form 101 PCT/IPEA/416

PCT Form 301 PCT/IPEA/409

PCT Form 304 1 sheet of formal drawings ((Fig. 1)

PCT Form 308 WO 01/06591 A1

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)	INTERNATIONAL APPLICATION NO. PCT/JP00/04793			ATTORNEY'S DOCKET NUMBER Y31-138999C/KK
24. The following fees are submitted:			CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00				
ENTER APPROPRIATE BASIC FEE AMOUNT =			\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).			<input type="checkbox"/> 20	<input type="checkbox"/> 30
			\$0.00	
CLAIMS		NUMBER FILED	NUMBER EXTRA	RATE
Total claims		11 - 20 =	0	x \$18.00 \$0.00
Independent claims		1 - 3 =	0	x \$84.00 \$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/> \$0.00	
TOTAL OF ABOVE CALCULATIONS =			\$890.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.			\$0.00	
SUBTOTAL =			\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).			<input type="checkbox"/> 20	<input type="checkbox"/> 30
			\$0.00	
TOTAL NATIONAL FEE =			\$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input checked="" type="checkbox"/> \$40.00	
TOTAL FEES ENCLOSED =			\$930.00	
			Amount to be: refunded	\$
			charged	\$

- A check in the amount of **\$930.00** to cover the above fees is enclosed.
- Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **50-0481** A duplicate copy of this sheet is enclosed.
- Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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NAME

34,386

REGISTRATION NUMBER

December 14, 2001

DATE

Y31-138999C/KK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of

Syuichi IZUCHI et al.

Serial No.: Not Yet Assigned

Group Art Unit: Not Yet Assigned

Filing Date: Concurrently Herewith

Examiner: Unknown

For: LITHIUM BATTERY

Assistant Commissioner of Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Prior to examination on the merits and calculation of the filing fee, please amend the above-identified application as follows:

IN THE CLAIMS:

Please amend the claims as follows:

3. (Amended) The lithium battery claimed in Claim 1, wherein said gel electrolyte is obtained by hardening a mixture of a liquid electrolyte and a monomer having at least two polymerizable functional groups in its molecular chain.

4. (Amended) The lithium battery claimed in Claim 1, wherein said lithium salt comprises LiBF_4 .

5. (Amended) The lithium battery claimed in Claim 1, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

Please add claims 6 - 11 as follows:

- - 6. (New) The lithium battery claimed in Claim 2, wherein said gel electrolyte is obtained by hardening a mixture of a liquid electrolyte and a monomer having at least two polymerizable functional groups in its molecular chain.

7. (New) The lithium battery claimed in Claim 2, wherein said lithium salt comprises LiBF_4 .

8. (New) The lithium battery claimed in Claim 3, wherein said lithium salt comprises LiBF_4 .

9. (New) The lithium battery claimed in Claim 2, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

10. (New) The lithium battery claimed in Claim 3, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

11. (New) The lithium battery claimed in Claim 4, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight. - -

REMARKS

Claims 3, 4, and 5 have been amended to delete multiple-dependency and claims 6-11 have been added accordingly.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned "Version with markings to show changes made."

Early, favorable prosecution on the merits is respectfully requested.

Please charge any deficiencies in fees and credit any overpayment of fees to Attorney's Deposit Account No. 50-0481.

Respectfully submitted,

Sean M. McGinn
Registration No.: 34,386

Date: December 14, 2001
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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the claims:

3. (Amended) The lithium battery claimed in Claim 1 [or 2], wherein said gel electrolyte is obtained by hardening a mixture of a liquid electrolyte and a monomer having at least two polymerizable functional groups in its molecular chain.

4. (Amended) The lithium battery claimed in [any one of Claims 1 to 3] Claim 1, wherein said lithium salt [is] comprises LiBF₄.

5. (Amended) The lithium battery claimed in [any one of Claims 1 to 4] Claim 1, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

Description

LITHIUM BATTERY

<Technical Field>

The present invention relates to a lithium battery and more particularly to improvements in gel electrolyte for use in the positive electrode, negative electrode or separator of lithium battery.

<Background Art>

In recent years, portable apparatus such as portable telephone, PHS and small-sized personal computer have shown a remarkable tendency toward the reduction of size and weight with the development of electronics technique. Thus, batteries which are used as power supply for these apparatus have been required to have a smaller size and weight.

One of batteries which can be expected for such a purpose is a lithium battery. In addition to primary lithium batteries which have been already put to practical use, secondary lithium batteries have been required to come into the market and have a higher capacity and a prolonged life.

Since the foregoing various lithium batteries use a liquid electrolyte as its ionically-conductive material, all these lithium batteries are mostly in a cylindrical or prismatic form using a metallic can having a thick wall.

Thus, a thin type lithium battery can be difficultly produced. Therefore, a thin type primary lithium battery using a thin metal foil has been put to practical use by a preparation process involving the use of a solid electrolyte instead of conventional liquid electrolyte and the application of printing technique. Applying these techniques, various researches and developments have heretofore been made also for the realization of practical use of thin type secondary lithium battery using a gel electrolyte.

A cylindrical or prismatic secondary lithium battery is prepared by such a process that an electrode group made of positive electrodes, negative electrodes and separators is inserted in a cylindrical or prismatic battery case, and then a liquid electrolyte is injected into the battery case. On the contrary, a secondary gel electrolyte lithium battery is prepared by such a process that a positive electrode and a negative electrode are opposed to each other with a gel electrolyte provided interposed therebetween, and then those electrodes are packed and thus has an advantage in production. However, this gel electrolyte battery is disadvantageous in that it has deteriorated high rate charge and discharge performance and low temperature performance as compared with the cylindrical or prismatic battery.

This disadvantage is attributed to the following

causes. Namely, the cylindrical or prismatic battery uses an electrolyte which is liquid and thus can easily undergo diffusion of lithium ion in the electrode and separator. On the contrary, since the gel electrolyte battery uses an electrolyte which is gel, the polymer contained in the electrolyte restricts the migration of ion, reducing the diffusion speed and hence deteriorating the high rate charge and discharge performance and low temperature charge and discharge performance to disadvantage.

Thus, as typical gel electrolytes having an enhanced lithium ion conductivity there have heretofore been widely studied gel electrolytes obtained by using a polyethylene oxide as a polymer skeleton and adding a liquid electrolyte made from lithium salts and organic solvents thereto. By predetermining the mixing ratio to lithium salts or to organic solvents, a lithium ion conductivity on the order of 1×10^{-3} S/cm, which stands with comparison with that of liquid electrolyte, has been realized so far. A lithium battery comprising such gel electrolytes has substantially been put to practical use.

However, the foregoing lithium battery using a gel electrolyte represented by polyethylene oxide is disadvantageous in that it exhibits a sufficient battery performance during low rate discharge but still shows a slow diffusion of lithium ion during high rate discharge, making it difficult to keep the battery performance at a

sufficient level.

The present invention has been worked out in the light of the foregoing problems. An object of the present invention is to provide a lithium battery which exhibits a gel electrolyte ion conductivity kept at a high level and allows smooth migration of lithium ion in the gel electrolyte without the necessity of any special production step to keep its performance at a sufficient level even during high rate discharge and have a prolonged life and a stable battery performance.

<Disclosure of the Invention>

In order to solve the foregoing problems, the present invention lies in a lithium battery having a power-generating element comprising at least a positive electrode, a negative electrode and a separator wherein a gel electrolyte comprising at least a polymer and a liquid electrolyte is used in at least a part of the power-generating element, characterized in that the concentration of lithium salt in the liquid electrolyte is from 1.5 to 5 mols per l of the liquid electrolyte. The present invention is also characterized in that the weight fraction of the polymer constituting the gel electrolyte comprising at least a polymer and a liquid electrolyte is from 5 to 30% by weight based on the sum of the weight of the polymer and the liquid electrolyte. The present invention is further characterized in that the gel electrolyte is

obtained by hardening a mixture of a liquid electrolyte and a monomer having at least two polymerizable functional groups in its molecular chain. The present invention is further characterized in that the lithium salt is LiBF₄. The present invention is further characterized in that the organic solvent constituting the liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

In other words, as a result of their extensive studies, the inventors found that the use of a gel electrolyte comprising a liquid electrolyte having a lithium salt dissolved therein in a concentration as high as about twice or more than the ordinary salt concentration of liquid electrolyte for lithium battery and a polymer makes it possible to obtain a good high rate discharge performance. Thus, the present invention has been worked out. In other words, the present invention lies in a lithium battery, characterized in that the concentration of lithium salt in the liquid electrolyte contained in at least one of positive electrode, negative electrode and separator is from 1.5 to 5 mols per l of the liquid electrolyte and the amount of the polymer is from 5 to 30% based on the weight of the polymer and the liquid electrolyte.

The concentration of lithium salt contained in the gel electrolyte is from 1.5 to 5 mols, preferably from 2 to

4 mols, more preferably from 2 to 3 mols per l of the liquid electrolyte. When the lithium salt concentration falls below 1.5 mols, the lithium ion concentration is small and the diffusion rate is small. When the lithium salt concentration exceeds 5 mols, the high salt concentration puts restrictions on the diffusion of lithium ion, reducing the diffusion rate of lithium ion and making it more likely that the precipitation of lithium salt can occur. The above defined range of salt concentration is preferred from the standpoint of difficulty in the precipitation of lithium salt.

Examples of the anion constituting the lithium salt which can be contained in the gel electrolyte include inorganic and organic anions. These lithium salts may be used singly or in combination of two or more thereof, as necessary. Examples of the inorganic anion include BF_4^- , PF_6^- , ClO_4^- , AsF_6^- , and SCN^- . Examples of the organic anion include $\text{C}_n\text{F}_{2n+1}\text{SO}_3^-$ ($n = 0$ to 5), $\text{C}(\text{SO}_2\text{C}_n\text{F}_{2n+1})(\text{SO}_2\text{C}_m\text{F}_{2m+1})(\text{SO}_2\text{C}_p\text{F}_{2p+1})^-$ ($n, m, p = 0$ to 5), $\text{N}(\text{SO}_2\text{C}_n\text{F}_{2n+1})(\text{SO}_2\text{C}_m\text{F}_{2m+1})^-$ ($n, m = 0$ to 5), and RCOO^- . Examples of R include groups represented by each of chemical formulae CH_3^- , $\text{OCOCH}=\text{CH}^-$, $\text{OCO-C}_6\text{H}_4^-$, and C_6H_5^- . Preferred among these lithium salts is LiBF_4 because it exhibits a good thermal stability and gives little problem of production of HF due to hydrolysis caused by the contamination by water.

Examples of the organic solvent to be contained in the gel electrolyte include lactones { γ -butyrolactone, γ -valerolactone, etc.}, chain esters {methyl acetate, methyl propionate, ethyl propionate, etc.}, carbonic acid esters {ethylene carbonate, propylene carbonate, diethyl carbonate, methyl ethyl carbonate, dimethyl carbonate, diphenyl carbonate, etc.}, cyclic ethers {tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolan, etc.}, chain ethers {1,2-dimethoxyethane, ethylene glycol methyl ethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, polyethylene glycol di(C_1-C_4) alkylether having a polymerization degree of 3 or more, propylene glycol dimethyl ether, polypropylene glycol di(C_1-C_4) alkylether having a polymerization degree of 2 or more, etc.}, N-methyloxazolidinone, sulfolanes {sulfolane, 2-methylsulfolane, etc.}, nitriles {acetonitrile, etc.}, sulfoxides {dimethyl sulfoxide, etc.}, amides {N,N-dimethylformamide, etc.}, and pyrrolidones {N-methylpyrrolidone, etc.}. These organic solvents may be used singly or in combination of two or more thereof as necessary. Preferred among these organic solvents are γ -butyrolactone, propylene carbonate, and ethylene carbonate from the standpoint of high dielectric constant, low vapor pressure and low flash point. An organic solvent containing γ -butyrolactone in an amount of not smaller than 50% by weight is even more preferable because it gives a

good high rate discharge performance when combined with a LiBF₄ salt having a good thermal stability.

The amount of the polymer to be contained in the gel electrolyte is preferably from 5% to 30%, more preferably from 10% to 25% based on the sum of the weight of the polymer and the liquid electrolyte. The polymer to be used in the gel electrolyte is not particularly limited. In general, however, it preferably swells somewhat in the liquid electrolyte. Examples of these polymers include acryloyl-based polymer, polyvinylidene fluoride, polyacrylonitrile, etc. Further, polymers obtained by the polymerization of monomers having a polymerizable functional group and soluble in the liquid electrolyte are preferred. Referring further to the foregoing gel electrolyte, it is preferably one obtained by hardening a mixture of a lithium salt, an organic solvent and a monomer having at least two polymerizable functional groups in its molecular chain.

Examples of the foregoing monomer having two or more polymerizable functional groups in its molecular chain include bifunctional (meth)acrylate {ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate having a polymerization degree of 2 or more, polypropylene glycol di(meth)acrylate having a polymerization degree of 2 or more, di(meth)acrylate of polyoxyethylene/polyoxypropylene

copolymer, butanediol di(meth)acrylate, hexamethylene glycol di(meth)acrylate, etc.}, trifunctional (meth)-acrylate {trimethylolpropane tri(meth)acrylate, glycerin tri(meth)acrylate, tri(meth)acrylate of ethylene oxide adduct of glycerin, ethylene oxide of glycerin, tri(meth)acrylate of propylene oxide adduct, etc.}, tetrafunctional or higher (meth)acrylate {pentaerythritol tetra(meth)acrylate, diglycerin hexa(meth)acrylate, etc.}, etc. Further, monomers having the structure represented by the following chemical formula 1, 2 or 3 can be used.

Examples of the positive active material to be used in the invention include cobalt-based compounds such as LiCoO_2 , nickel-based compounds such as LiNiO_2 , manganese-based compounds such as LiMn_2O_4 , titanium-based compounds such as lithium titanium oxide, vanadium-based compounds such as vanadium oxide-based active material, iron-based compounds such as iron phosphate-based active material, etc., but the present invention is not limited thereto. Examples of the negative active material include lithium metal, lithium alloy, and carbon-based compound such as graphite, but the present invention is not limited thereto.

In accordance with the invention, the following effects can be expected. Firstly, since the concentration of lithium salt in the gel electrolyte is high, polarization accompanying the migration of lithium ion can be relaxed during high rate discharge, providing a good

charge and discharge performance.

Secondly, since the concentration of lithium salt in the positive electrode, negative electrode and separator is enhanced with respect to the organic solvent, the vapor pressure of the organic solvent in the electrolyte can fall, making it possible to inhibit the evaporation of the organic solvent that causes ignition.

Accordingly, in accordance with the invention, the following effects can be synergistically exerted, making it easy to provide a lithium battery excellent in reliability as well as in initial capacity, high rate charge and discharge performance, low temperature performance and safety.

<Brief Description of the Drawings>

Fig. 1 illustrates a sectional view of the lithium battery of the invention.

The reference numerals 1, 2, 3, 4, 5 and 6 in Fig. 1 indicate a positive composite, a negative composite, a positive electrode current collector, a negative electrode current collector, a separator, and an aluminum laminate film.

<Best Mode for Carrying Out the Invention>

The present invention will be further described with reference to the following examples. The term "electrolyte solution" as used herein is meant to indicate a mixture of

a liquid electrolyte having lithium salts dissolved in organic solvents and monomers having two or more polymerizable functional groups in its molecular chain. In the case where the polymer constituting the gel electrolyte is one obtained by the polymerization of a monomer having two or more polymerizable groups in its molecular chain as in the present example, the weight fraction of the polymer to the gel electrolyte corresponds to that of the monomer to the electrolyte solution.

(Example 1)

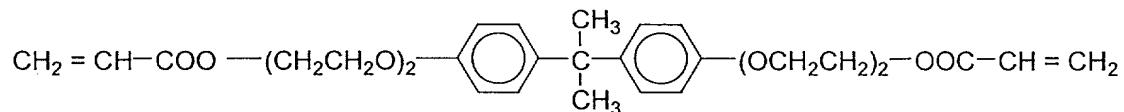
Fig. 1 illustrates a sectional view of the lithium battery of the invention. 1 indicates a positive composite mainly comprising lithium cobalt oxide as a positive active material. The positive composite is applied to a positive electrode current collector 3 made of aluminum foil. 2 is a negative composite mainly comprising carbon as a negative active material. The negative composite is applied to a negative electrode current collector 4 made of copper foil. The positive composite 1 and the negative composite 2 are laminated with a separator 5 made of gel electrolyte provided interposed therebetween. The electrode group thus laminated is covered by an aluminum laminate film 6 which is then heat-fused at four sides thereof to prepare a lithium battery.

A process for the preparation of a lithium battery having the foregoing structure will be described

hereinafter. The positive composite 1 was obtained as follows. Firstly, a mixture of lithium cobalt oxide as a positive active material, acetylene black as an electrically-conducting material and a 6.6 wt% N-methyl-2-pyrrolidone solution of a polyvinylidene fluoride as a binder (lithium cobalt oxide : acetylene black : polyvinylidene fluoride = 91 : 4.5 : 4.5 (by weight)) was applied to an aluminum foil (thickness: 15 μm) as the positive electrode current collector 3, and then dried. The coated aluminum foil was then pressed until the thickness of the composite layer reached 0.1 mm to obtain a positive active material sheet. Subsequently, a liquid electrolyte having 2.2 mols of LiBF₄ dissolved in 1 l of γ -butyrolactone was mixed with an acrylate monomer having the structure represented by the chemical formula 1 in an amount of 15% based on the sum of the weight of the liquid electrolyte and the monomer to prepare an electrolyte solution. The foregoing positive active material sheet was then dipped in the electrolyte solution so that it was vacuum-impregnated with the electrolyte solution. Subsequently, the positive active material sheet was withdrawn from the electrolyte solution, and then irradiated with electron beam so that the monomer was subjected to polymerization to form a polymer. In this manner, the positive composite 1 was obtained. The negative composite 2 was obtained in the same manner as the

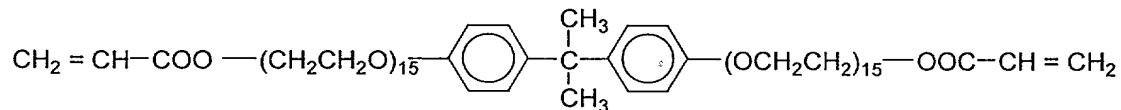
positive composite 1 except that carbon was used as a negative active material and a copper foil (thickness: 10 μm) was used as a negative electrode current collector 4.

Chemical formula 1



The separator 5 was obtained as follows. Firstly, a liquid electrolyte having 2.2 mols of LiBF_4 as a lithium salt dissolved in 1 l of γ -butyrolactone as an organic solvent was mixed with a bifunctional acrylate monomer having the structure represented by the following chemical formula 2 in an amount of 10% based on the sum of the weight of the liquid electrolyte and the monomer. The mixture was applied to the positive composite 1, and then irradiated with electron beam so that the monomer was subjected to polymerization to form a polymer. Thus, a gel electrolyte separator was prepared.

Chemical formula 2



A battery was prepared as a battery A1 of the invention from the foregoing starting materials according to the foregoing preparation process.

(Example 2)

A battery was prepared as a battery A2 of the invention in the same manner as the battery A1 of the invention except that a liquid electrolyte having 1.5 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Example 3)

A battery was prepared as a battery A3 of the invention in the same manner as the battery A1 of the invention except that a liquid electrolyte having 3 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Example 4)

A battery was prepared as a battery A4 of the invention in the same manner as the battery A1 of the invention except that a liquid electrolyte having 4 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Example 5)

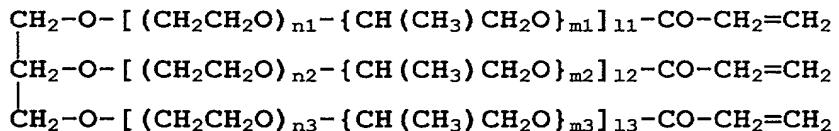
A battery was prepared as a battery A5 of the invention in the same manner as the battery A1 of the invention except that a liquid electrolyte having 5 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone

was used in the step of producing positive electrode, negative electrode and separator.

(Example 6)

A battery was prepared as a battery C1 of the invention in the same manner as the battery A1 of the invention except that a trifunctional acrylate monomer (weight-average molecular weight: approx. 8,000) having the structure represented by the chemical formula 3 was used instead of the bifunctional acrylate monomer to be used in the preparation of separator 5.

Chemical formula 3



(wherein n1, n2, n3, m1, m2 and m3 each represents an integer of not smaller than 0)

(Example 7)

A battery was prepared as a battery C2 of the invention in the same manner as the battery C1 of the invention except that a liquid electrolyte having 3 mols of LiBF₄ as a lithium salt dissolved in 1 l of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Example 8)

A battery was prepared as a battery E1 of the invention in the same manner as the battery A1 except that the content of the monomer in the electrolyte solution with

which the positive active material sheet is vacuum-impregnated is 5% based on the sum of the weight of the liquid electrolyte and the monomer and the content of the monomer in the electrolyte solution to be used in the separator is 5% based on the sum of the weight of the liquid electrolyte and the monomer.

(Examples 9 to 15)

Batteries E2 to E8 of the invention were prepared by changing the content of the monomer in the electrolyte solution with which the positive active material sheet is vacuum-impregnated and the content of the monomer in the electrolyte solution to be used in the separator as set forth in Table 4 similarly to Example 8.

(Comparative Example 1)

A battery was prepared as a comparative battery B1 in the same manner as the battery A1 of the invention except that a liquid electrolyte having 1.2 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Comparative Example 2)

A battery was prepared as a comparative battery B2 in the same manner as the battery A1 of the invention except that a liquid electrolyte having 6 mols of LiBF₄ as a lithium salt dissolved in 1 ℥ of γ -butyrolactone was used in the step of producing positive electrode, negative

electrode and separator.

(Comparative Example 3)

A battery was prepared as a comparative battery D1 in the same manner as the battery C1 of the invention except that a liquid electrolyte having 1.2 mols of LiBF₄ as a lithium salt dissolved in 1 l of γ -butyrolactone was used in the step of producing positive electrode, negative electrode and separator.

(Comparative Example 4)

A battery was prepared as a battery F1 of the invention in the same manner as the battery A1 except that the content of the monomer in the electrolyte solution with which the positive active material sheet is vacuum-impregnated is 4% based on the sum of the weight of the liquid electrolyte and the monomer and the content of the monomer in the electrolyte solution to be used in the separator is 4% based on the sum of the weight of the liquid electrolyte and the monomer.

(Comparative Example 5)

A battery was prepared as a comparative battery F2 in the same manner as the battery F1 of the invention except that the content of the monomer in the electrolyte solution was 35%.

Subsequently, the batteries A1 to A5 of the invention and the comparative batteries B1 and B2 were each charged to a terminal voltage of 4.2 V with a current of 1 mA

(corresponding to 10 hour rate) at a temperature of 20°C, and then discharged to 2.7 V at a high rate with a constant current of 20 mA (corresponding to 0.5 hour rate). These batteries were each then measured for discharge capacity. The results are set forth in Table 1.

Table 1

	Designation of battery	Lithium salt concentration (mol/l)	20°C, 20mA discharge capacity (mAh)
Example 1	A1	2.2	4.0
Example 2	A2	1.5	2.5
Example 3	A3	3.0	4.5
Example 4	A4	4.0	3.0
Example 5	A5	5.0	1.8
Comparative Example 1	B1	1.2	1.2
Comparative Example 2	B2	6.0	0.3

As can be seen in the results of Table 1, the batteries A1 to A5 of the invention exhibit a higher discharge capacity than the comparative batteries B1 and B2.

Subsequently, the batteries A1 and A2 of the invention and the comparative battery B1 were each charged to a terminal voltage of 4.2 V with a current of 1 mA (corresponding to 10 hour rate) at a temperature as low as -20°C, and then discharged to 2.7 V with a constant current of 2 mA (corresponding to 5 hour rate). These batteries were each then measured for low temperature discharge capacity. The results are set forth in Table 2.

Table 2

	Designation of battery	Lithium salt concentration (mol/l)	-20°C, 2mA discharge capacity (mAh)
Example 1	A1	2.2	7.8
Example 2	A2	1.5	6.3
Comparative Example 1	B1	1.2	1.0

As can be seen in the results of Table 2, the batteries A1 and A2 of the invention exhibit an extremely high discharge capacity at low temperature as compared with the comparative battery B1.

Subsequently, the batteries C1 and C2 of the invention and the comparative battery D1 were each charged to a terminal voltage of 4.2 V with a current of 1 mA (corresponding to 10 hour rate) at a temperature of 20°C, and then discharged to 2.7 V at a high rate with a constant current of 20 mA (corresponding to 0.5 hour rate). These batteries were each then measured for discharge capacity. The results are set forth in Table 3.

Table 3

	Designation of battery	Lithium salt concentration (mol/l)	20°C, 20mA discharge capacity (mAh)
Example 6	C1	2.2	7.8
Example 7	C2	3.0	6.6
Comparative Example 3	D1	1.2	1.6

As can be seen in the results of Table 3, the batteries C1 and C2 of the invention exhibit an extremely high discharge capacity as compared with the comparative battery D1. This demonstrates that the present invention can be applied even if the monomers constituting the gel are different.

Subsequently, the batteries E1 to E8 of the invention and the comparative batteries F1 and F2 were each charged to a terminal voltage of 4.2 V with a current of 1 mA (corresponding to 10 hour rate) at a temperature of 20°C, and then discharged to 2.7 V at a high rate with a constant current of 20 mA (corresponding to 0.5 hour rate). These batteries were each then measured for discharge capacity. The results are set forth in Table 4.

Table 4

	Designation of battery	Concentration of monomer in electrode (%)	Concentration of monomer in separator (%)	Lithium salt concentration (mol/l)	20°C, 20mA discharge capacity (mAh)
Example 1	A1	15	10	2.2	4.0
Example 8	E1	5	5	2.2	4.6
Example 9	E2	15	5	2.2	4.1
Example 10	E3	30	5	2.2	2.0
Example 11	E4	5	10	2.2	4.5
Example 12	E5	30	10	2.2	1.9
Example 13	E6	5	30	2.2	2.5
Example 14	E7	15	30	2.2	3.0
Example 15	E8	30	30	2.2	1.8
Comparative Example 4	F1	4	4	2.2	0 (short- circuited)
Comparative Example 5	F2	35	35	2.2	1.3

As can be seen in Table 4, the batteries A1 and E1 to E8 of the invention exhibit a good discharge capacity as compared with the comparative batteries F1 and F2. The concentration of the monomer in the electrode and the separator were varied from 4% to 35%. When the concentration of the monomer were each 4%, the separator became mechanically weak to cause short-circuiting and the solution oozed from the electrode, giving practical problems. When the concentration of the monomer were each 35%, there were too much polymer that retarded the ion diffusion, deteriorating the high rate performance and hence giving practical problems.

While a gel electrolyte was used not only in the separator but also in the electrolyte in the electrode in the present examples, the present invention does not restrict the form of the electrolyte in the electrode. Accordingly, even in the case where a liquid electrolyte is used as the electrolyte in the electrode for either or both of the positive electrode and negative electrode, the effect of the invention can be effectively exerted so far as the electrolyte in the separator is a gel electrolyte.

As the separator there may be used not only one obtained by the method described in the examples but also one obtained by a method comprising impregnating a porous substrate such as nonwoven cloth with an electrolyte solution, and then irradiating the porous substrate with

electron beam, which is laminated on the electrode for use.

<Industrial Applicability>

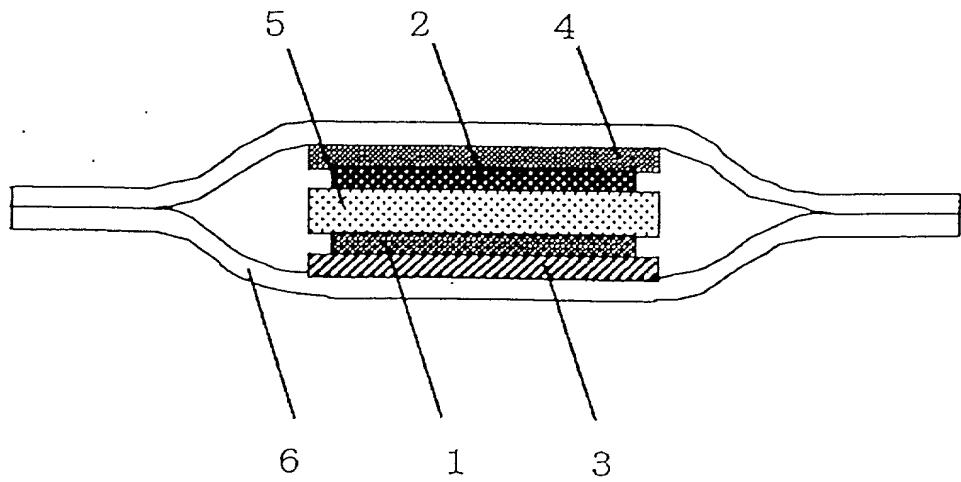
As mentioned above, in accordance with the present invention, a lithium battery excellent in initial capacity, high rate discharge performance, low temperature performance and cycle life performance can be provided without the necessity of any special production step.

Claims

1. A lithium battery having a power-generating element comprising at least a positive electrode, a negative electrode and a separator wherein a gel electrolyte comprising at least a polymer and a liquid electrolyte is used in at least a part of said power-generating element, characterized in that the concentration of lithium salt in said liquid electrolyte is from 1.5 to 5 mols per l of the liquid electrolyte.
2. The lithium battery claimed in Claim 1, wherein the weight fraction of the polymer constituting said gel electrolyte comprising at least a polymer and a liquid electrolyte is from 5 to 30% by weight based on the sum of the weight of said polymer and said liquid electrolyte.
3. The lithium battery claimed in Claim 1 or 2, wherein said gel electrolyte is obtained by hardening a mixture of a liquid electrolyte and a monomer having at least two polymerizable functional groups in its molecular chain.
4. The lithium battery claimed in any one of Claims 1 to 3, wherein said lithium salt is LiBF₄.
5. The lithium battery claimed in any one of Claims 1 to 4, wherein the organic solvent constituting said liquid electrolyte contains γ -butyrolactone in an amount of not smaller than 50% by weight.

10/018020

FIG. 1



Application for United States Patent

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

LITHIUM BATTERY

the specification of which:
(check one)

(is attached hereto)
____ was filed on _____
as Application Serial No. _____
and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56*

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

P.Hei. 11-205528 (Number)	Japan (Country)	21/July/1999 (Day/Month/Year Filed)	priority claimed <input checked="" type="checkbox"/>	yes	no
P.2000-141286 (Number)	Japan (Country)	15/May/2000 (Day/Month/Year Filed)	<input checked="" type="checkbox"/>	yes	no

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Filing Date) (Status: patented, pending, abandoned)

Power of Attorney: As a named inventor, I hereby appoint Sean M. McGinn, Reg. No. 34,386, and Frederick W. Gibb, III, Reg. No. 37,629, as attorneys and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. All correspondence should be directed to McGinn & Gibb, PLLC, 8321 Old Courthouse Road, Suite 200, Vienna, Virginia 22182-3817. Telephone calls should be directed to McGinn & Gibb, PLLC at (703) 761-4100.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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(An additional sheet(s) is/are attached hereto if the present invention includes more than four inventors.)

cont'd

*Title 37, Code of Federal Regulations, § 1.56:

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith toward the Patent and Trademark Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is canceled or withdrawn from consideration, or the application becomes abandoned.

(b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made of record in the application, and (1) it establishes by itself or in combination with other information, a prima facie case of unpatentability; or (2) it refutes, or is inconsistent with, a position the applicant takes in: (i) opposing an argument of unpatentability relied on by the Office, or (ii) asserting an argument of patentability.

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Citizenship _____

Post Office Address _____

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